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Investigation of the relationship between CO₂ reservoir rock property change and the surface roughness change originating from the supercritical CO₂-sandstone-groundwater geochemical reaction at CO₂ sequestration condition

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Abstract

Laboratory experiments were performed to investigate the property change of sandstones, resulting from scCO₂-rock-groundwater reaction for 150 days under CO₂ sequestration conditions. The average surface roughness value (SR_{rms}) increased more than 3.5 times during early 90 days, suggesting that the weathering process of sandstone occurs in the early reaction time after CO₂ injection. The average porosity of sandstones increased by 8.8 % and P wave velocity decreased by 5.7 %. The trend of rock property change and SR_{rms} change showed in a logarithmic manner, indicating that the physical property change of reservoir rocks directly comes from CO₂ related geochemical reaction.

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1. Introduction

Geological sequestration for CO₂ capture and storage is considered to be one of the available technologies to reduce

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CO₂ emissions [1, 2, 3]. It is agreed that before implementing CO₂ sequestration technology on a large scale, the confirmation of its viability regarding injection amount and long-term safety for both humans and the environment is crucial. Various laboratory scale experiments have been performed to get meaningful information about what happens in CO₂ sequestration sites, but most of them were limited to the qualitative investigation for the mineral or rock property changes under CO₂ sequestration condition [4, 5, 6].

From previous researches, it was suggested that the supercritical CO₂ (scCO₂) injected into the aquifer may accelerate the geochemical reaction among CO₂, groundwater, and rock, but that it will take a long time to change the rock property at the CO₂ sequestration site [7, 8, 9]. However, several recent studies cast doubt on whether the geochemical reaction rate including scCO₂ interaction is slow [6, 10, 11, 12]. If the geochemical reaction by injected scCO₂ is going faster than expected and thus becomes one of parameters controlling CO₂ storage, a quantitative understanding of the geochemical reaction is essential to estimate the long-term property changes of CO₂ reservoir rock. Even though several qualitative laboratory experiments were performed, a long-term quantification of the rock property change, resulting directly from the geochemical reaction, has almost never been attempted in previous studies. The lack of the quantification for these geochemical reaction comes from the difficulty to draw the parameters, representing the geochemical reaction occurred under CO₂ sequestration condition and also to find out the relationship between the geochemical reaction and the physical property changes of the rock. It's more important than ever to estimate the long term rock property changes originating from scCO₂-rock-groundwater reaction to search for the available aquifer as a CO₂ sequestration site and also to prevent accidental leaking of CO₂ from the storage site.

This study focused on the quantitative investigation of scCO₂-sandstone-groundwater reactions under CO₂ sequestration conditions. The relationship between the geochemical reaction and the physical rock property change was investigated to find out the successful subsurface CO₂ sequestration site. Results of this study will provide meaningful information to estimate the long-term property change of CO₂ reservoir rock and also to determine the favorite CO₂ injection site from the viewpoint of CO₂ capacity and safety.

2. Experimental and analytical methods

2.1. Preparation of sandstone and groundwater

The Gyeongsang basin is considered to be an available CO₂ sequestration site in Korea because of its large CO₂ storage capacity (1,011 megatons for only Sindong lithostratigraphic group in the Gyeongsang basin)[13]. In 2012, a drilling site for scCO₂ injection was determined and the continuous drill cores (6.8 cm of average diameter) from the surface to 1,200 m in depth were collected. Total 11 consolidated cylindrical sandstone cores (4.2 cm in diameter; 6 - 7 cm in length of each) without cracks or fractures were used for the experiment to quantify the physical property changes of sandstones after being reacted with scCO₂. In order to determine the mineral composition of sandstones before the experiment, a modal analysis was conducted to measure the portion of each mineral on the surface of each sandstone core. From the modal analysis, the sandstone mostly consisted of plagioclase, perthite, muscovite, biotite, calcite and chlorite, and their average proportions were 9.1, 25.0, 0.8, 1.5, 4.7 and 4.0 %, respectively. These minerals might control the geochemical reaction under the sequestration condition and five target minerals such as quartz, plagioclase, perthite, biotite and calcite were used for the experiment. Groundwater used for the experiment was sampled from the drilling site (800 m in depth). Table 1 shows results for groundwater quality analysis.

Table 1. Chemical properties and ions concentration of groundwater used in experiments

Temp. (°C)	pH	Concentration (mg/L)										
		Fe ²⁺	Si ⁴⁺	Al ³⁺	Mg ²⁺	K ⁺	Ca ²⁺	Na ⁺	HCO ₃ ⁻	SO ₄ ²⁻	Cl ⁻	NO ₃ ⁻
40.0	8.6	0.0	7.6	4.8	20.9	23.3	544.3	638.0	52.2	300.0	2105.0	293.7

2.2. Slab experiment for SR_{rms} measurement from the geochemical reaction

One flat surface of each sandstone core was cut into three thin slabs (1 cm x 1 cm x 0.2 cm each) for the surface roughness change experiment. One surface of each slab was polished with powdered diamond paper, and the other slab surface was attached with a glass slide plate. A stainless steel cell (purchased from Thar; a capacity of 130 ml) inner-coated with Teflon layer was connected by a high pressure CO_2 injection pump (Thar; P-50) and a back pressure regulator (Thar; Automated BPR). The inside of the cell was maintained at 100 bar by CO_2 injection control software (Thar; Injection control software). A hundred milliliters of groundwater was injected into the cell and each sandstone slab was immersed into groundwater in the cell. Void spaces of the cell were filled in with scCO_2 by the pump and the back pressure regulator, simulating the geochemical reaction that would occur in the CO_2 sequestration site (100 bar and 50 °C). The outer wall of each cell was covered with a heating jacket to maintain a constant temperature (50 °C). The scCO_2 -groundwater-sandstone reaction at 100 bar and 50 °C occurred in the cell for 150 days. Fig. 1 shows the procedure of the slab experiment.

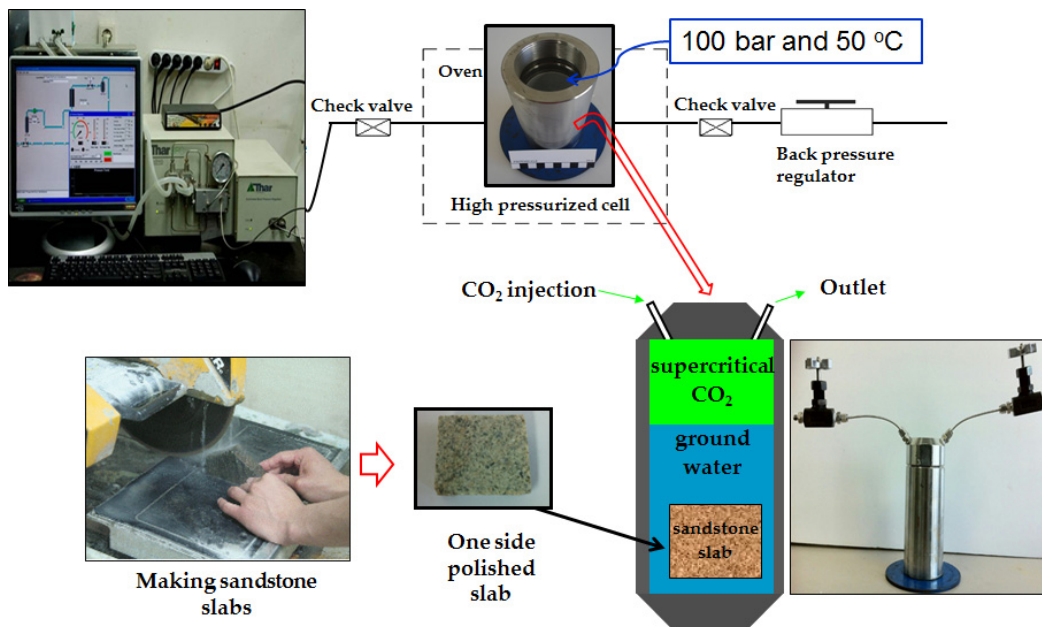


Fig. 1. Procedure of the slab experiment for the scCO_2 -sandstone-groundwater reaction.

For the surface roughness analysis of sandstone slabs, five representative minerals of slabs surface (quartz, plagioclase, perthite, biotite, and calcite) for each sandstone core were observed using a reflecting microscope (Olympus BX51), and three locations on each mineral surface were randomly selected for 2-dimensional surface images from SPM (Scanning Probe Microscope; MultiMode™ SPM) analysis at different reaction times. SPM includes a cantilever with a sharp tip at its end, which is used to scan the slab surface acquiring 2-dimensional images, measuring the displacement height in units of nanometers (nm) by scanning the sandstone slab surface with the cantilever tip point to point. To reduce all of the information in the 2-dimensional surface profile to a single number, several surface roughness parameters had been developed [14, 15]. In this study, the surface roughness value (SR_{rms}) of each thin sandstone slab was calculated from SPM analytical data, specifically by the RMS (root mean square) value between the reference height (Z_o = the mean line from all points) and the height of each point on the surface [15](Fig. 2). The formula to calculate SR_{rms} (unit: nm) is shown below;

$$SR_{rms} = \sqrt{\frac{1}{n} \sum_{i=1}^n y_i^2} \quad (1)$$

where, n is equally spaced point number (262,144) of the surface area and y_i (ΔZ in Fig.2) is the vertical distance from the mean line (Z_0) to the i^{th} point. Three different locations were randomly selected on each mineral surface of the slab and an area of $50 \mu\text{m} \times 50 \mu\text{m}$ around each location (a total of 262,144 points (512×512) on each selected area) was used to calculate SR_{rms} . The average SR_{rms} for three different locations representing the surface roughness value for each mineral of the sandstone slab was used to quantify the mineral surface weathering process that occurred on the slab surface by scCO_2 –sandstone–groundwater reaction. All average SR_{rms} values for sandstone slabs were plotted with different reaction time; the trend of the change of SR_{rms} for sandstones was compared with the trend of physical property change of sandstones; and results might derive out further than a quantitative relationship between SR_{rms} and rock property change.

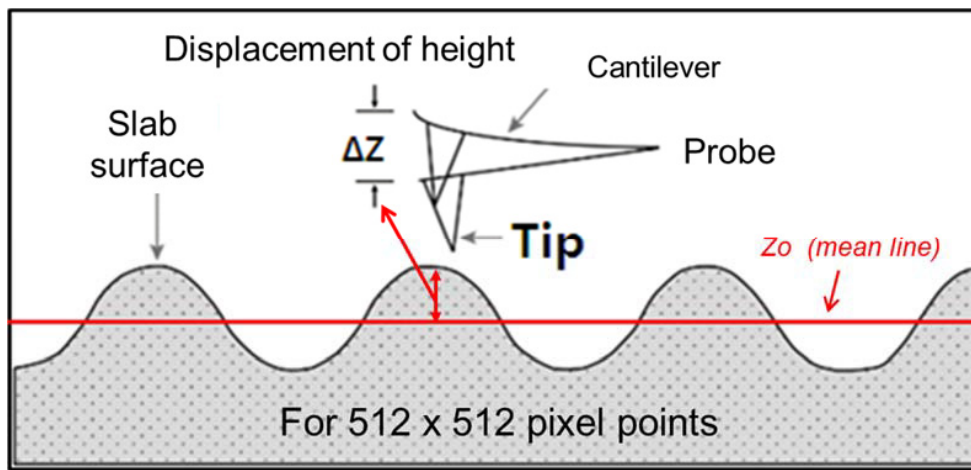


Fig.2. Principle to calculate the surface roughness value (SR_{rms}) from SPM analysis.

2.3. Sandstone core experiment for physical property change

The quantitative measurement for physical property changes of sandstones originating from scCO_2 injection in pore spaces is very important because the rate of these property changes directly affect not only the storage capacity of CO_2 but also the safety of injected CO_2 [16]. For the experiments to quantify the physical property changes of sandstone cores, total 11 cylindrical sandstone cores (4.2 cm in diameter; 5 - 6 cm in length each) were prepared. A large stainless steel chamber (18 cm in diameter; 2.2 liter of capacity) was used to simulate the temperature and pressure conditions (50 °C and 100 bar) of CO_2 sequestration. Two liters of groundwater was added to the Teflon coated stainless chamber, and each sandstone core was immersed in groundwater. The void space of the chamber was filled with scCO_2 , maintaining 100 bar and 50 °C. At a certain reaction time interval (total 150 days of reaction), physical properties of sandstone cores (total 11 cores: S1-1~S3-3) were measured to investigate the effect of scCO_2 on the reservoir rock (sandstone). To measure its physical properties, each sandstone core was taken from the cell; it was dried at 50 °C for 48 hour. Physical properties of cores such as dry density, porosity, seismic velocity and dynamic Young's modulus were measured by 'ISRM (International society for rock mechanics) suggested Method-1981', 'ASTM/D2845-05' test, and 'ASTM/D3148-02' test referred from the American Society of Testing Materials. The

experiment with the control sandstone core without scCO₂ in the cell (immersed in only groundwater at 100 bar and 50 °C) was repeated to consider only the effect of scCO₂ injection on the physical property changes. The property values of sandstone cores vs. the reaction time were plotted to calculate the property change rate; their trends were compared with those of SR_{rms} for the same sandstone cores. Fig. 3 shows the procedure of the sandstone core experiment.

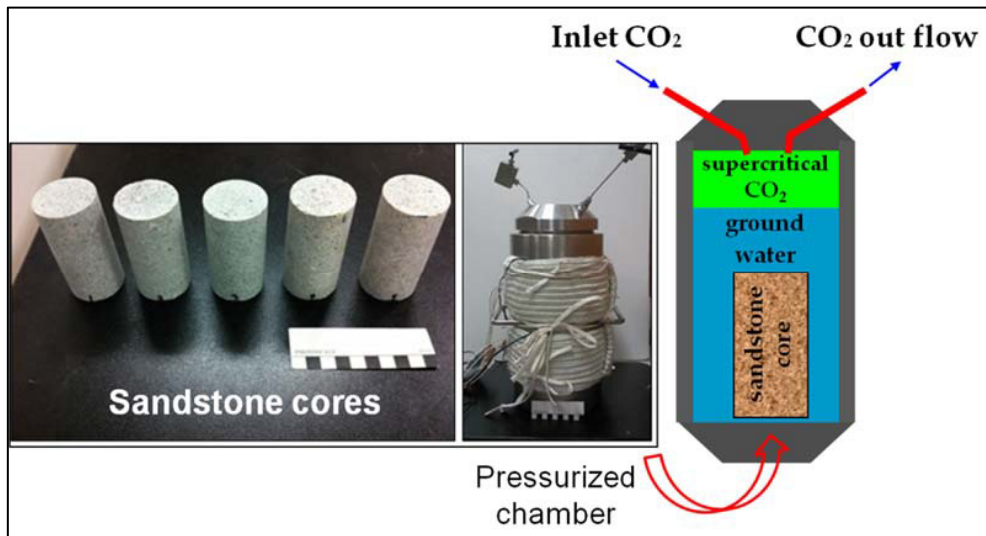


Fig. 3. Core experiments to measure physical property changes of the sandstone.

3. Results and discussion

3.1. Slab experiment for SR_{rms} measurement from the geochemical reaction

The average surface roughness values (SR_{rms}) of minerals for three sandstone slabs (S1, S2, and S3) at different reaction time are shown in Fig. 4. The SR_{rms} increase for minerals during the reaction presented a non-linear pattern (the logarithmic increase curve), suggesting that the geochemical weathering process occurred fast in the early reaction times (within 60 days) and it became stable after 60 days. The average SR_{rms} for plagioclases in three sandstones increased by 8.4 times during 90 days of reaction and 2.9 and 1.7 times for quartz and biotite, respectively. The possible rate of surface roughness change for each sandstone by scCO₂-rock-groundwater reaction could be achieved from the logarithmic equation, resulting from the curve fitting in Fig. 4 and the equation was shown below;

$$SR_{rms}(t) = a \ln(t) + b \quad (2)$$

where, t is the reaction time (day); a is the rate of surface roughness change; b is the intercept constant. The average values for a and b of sandstone and for mineral were in Table 2.

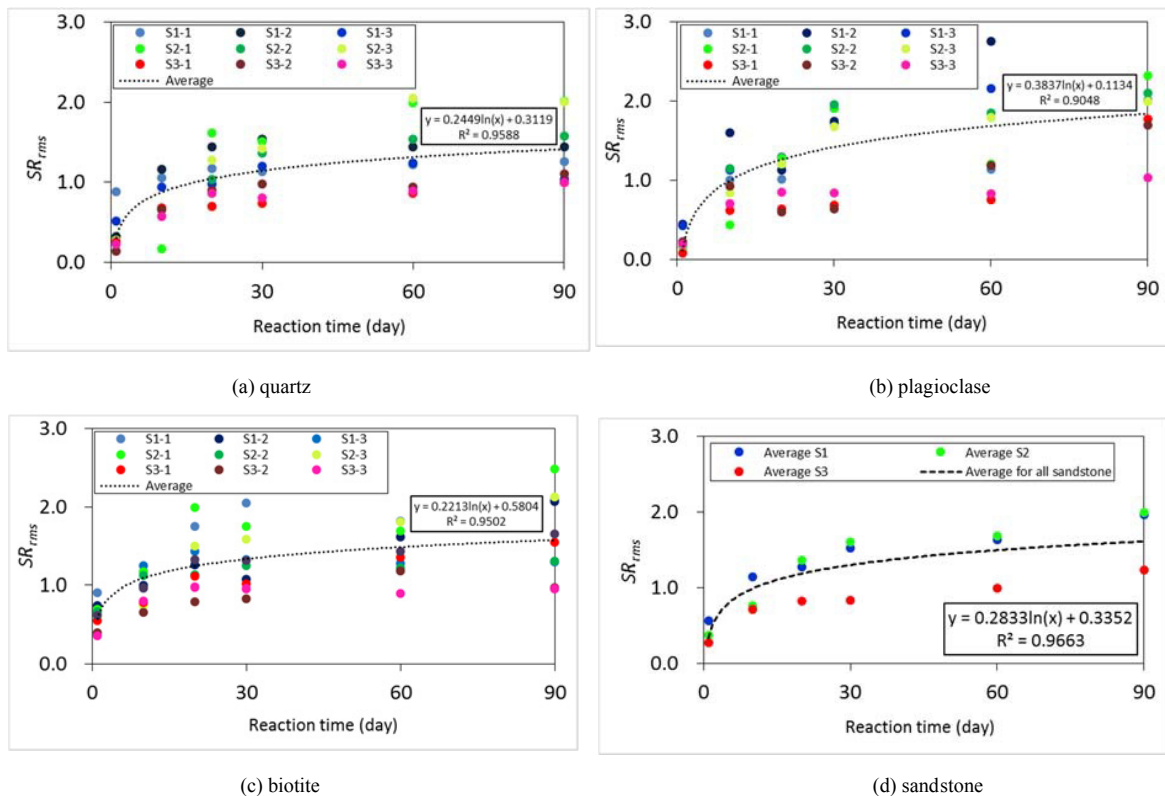


Fig. 4. Results of SR_{rms} (x 100 nm) change for minerals in sandstone by $scCO_2$ -rock-groundwater reaction.

Table 2. Constants of equation (2) fitted from SR_{rms} vs. reaction time for three sandstones.

Slab surface	Rate constant of surface roughness change (a)	Intercept constant (b)	R^2 for the fitted curve
Quartz	0.2449	0.3119	0.9588
Plagioclase	0.3837	0.1134	0.9048
Biotite	0.2213	0.5804	0.9502
S1	0.2921	0.5081	0.9635
S2	0.3640	0.2459	0.9219
S3	0.1937	0.2517	0.9581
Total sandstone	0.2833	0.3352	0.9663

3.2. Sandstone core experiment for physical property change

Fig.5 shows results of average changes in the physical properties of three sandstone cores (S1, S2 and S3) during 150 days of the supercritical CO_2 -groundwater-sandstone reaction. The average porosity of the sandstone cores was 8.183 % before the reaction and it increased to 8.906 % after 60 days of the reaction (8.84 % of increase). The average dry density of the cores decreased from 2.390 g/cm³ to 2.384 g/cm³. The average P-wave and S-wave velocity of the cores also decreased from 3,578 m/sec and 1,288 m/sec to 3,375 m/sec and 1,214 m/sec, respectively. These results suggested that the decrease of seismic velocity of sandstones is associated with the porosity increase, resulting from

the dissolution during the reaction. The average uniaxial compression strength for the sandstone cores was 52.23 MPa and it decreased to 44.81 MPa during 60 days reaction, suggesting that the compression strength of the sandstone decreased considerably, because of micro-cracks and perforation produced by the dissolution, which were observed by SEM and SPM analyses. The pattern of physical property changes for the cores was similar to that of the SR_{ms} increase, following the first order reaction with reaction time (logarithmic pattern).

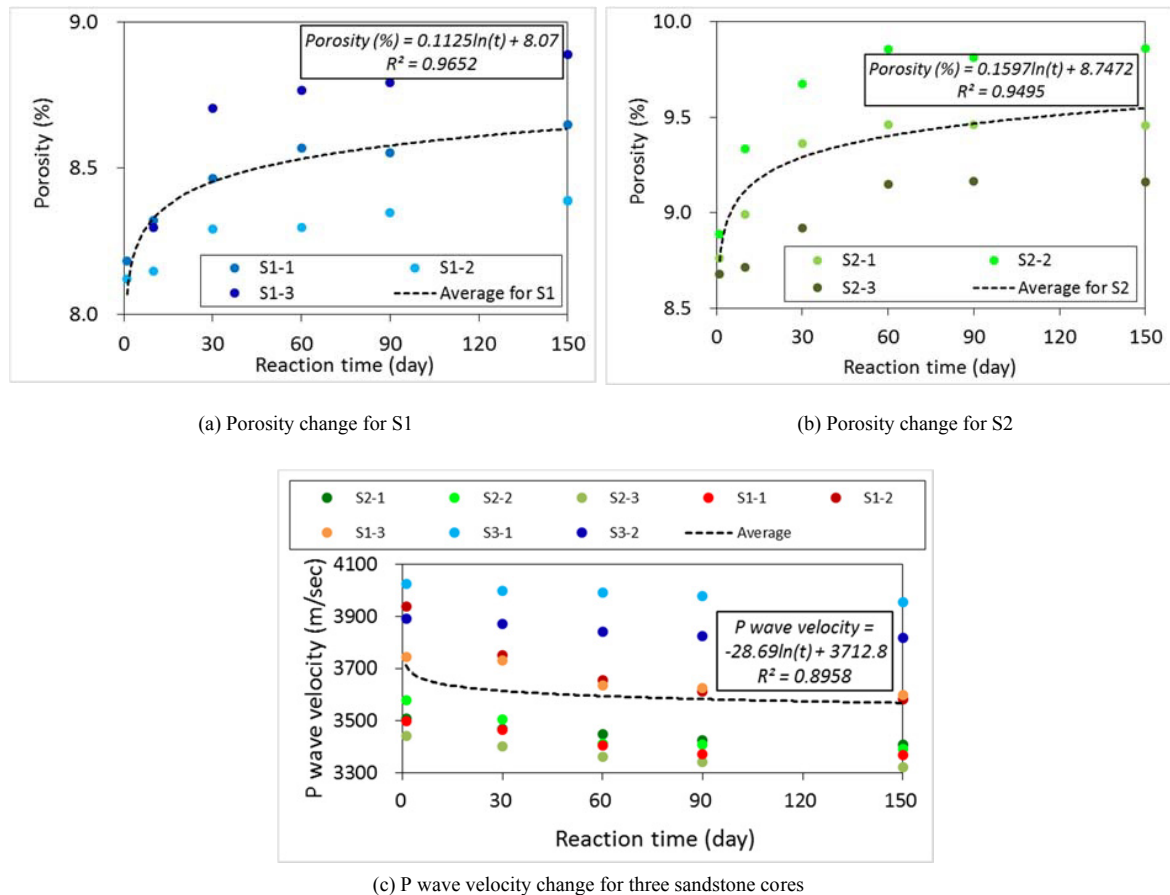


Fig. 5. Results of physical property change for the sandstone during the $scCO_2$ -rock-groundwater reaction.

4. Conclusion

Laboratory scale experiments successfully demonstrated that a supercritical CO_2 -sandstone-groundwater reaction occurs within a short time, and not only leads to the surface roughness change and dissolution/precipitation of minerals but also to physical property changes, controlling the movement of CO_2 in reservoir rocks. The active dissolution of Ca-feldspar and calcite in sandstones of the Gyeongsang basin occurred with the reaction, and during 60 days reaction the average porosity of the sandstones rose 8.8 %, and P wave velocity was down 5.7 %. Results of this study suggested that the geochemical weathering process, dominated by dissolution following CO_2 injection, is not a stable parameter and it should be considered when determining injection sites for safe CO_2 sequestration. Results of this study will provide meaningful information for the future decision regarding CO_2 injection sites at Gyeongsang basin, Korea.

5. Acknowledgements

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